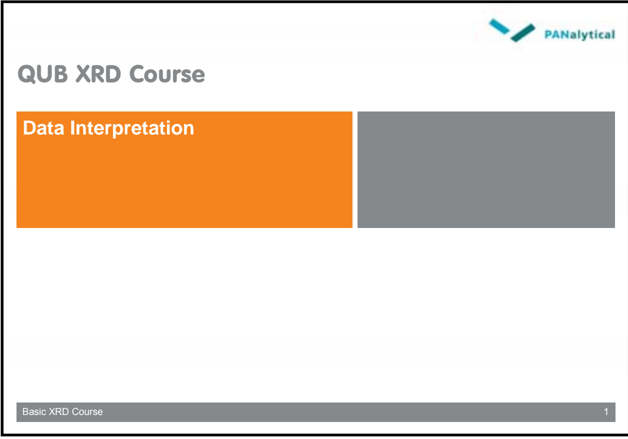
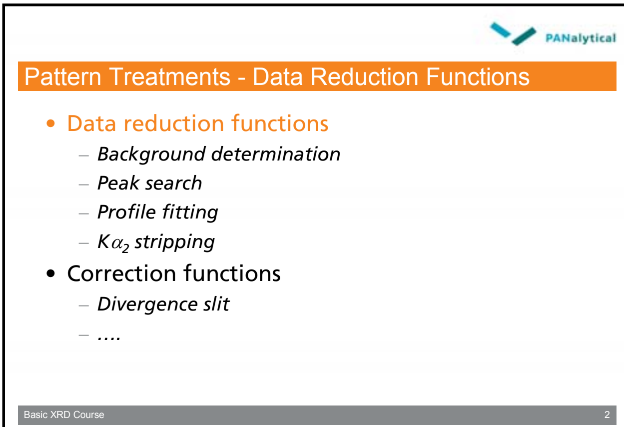
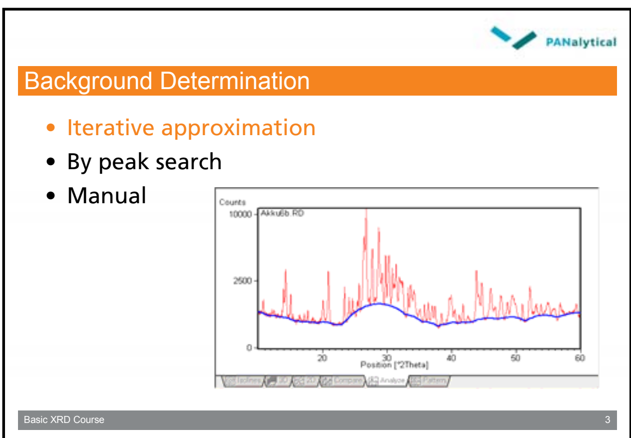
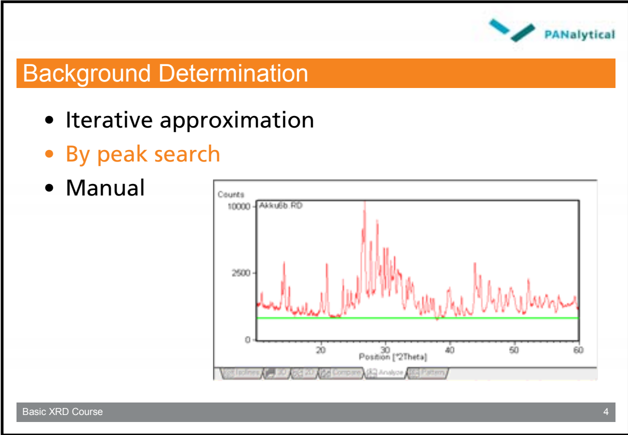
Identification with X'Pert HighScore: Search-match and Identification Background Information

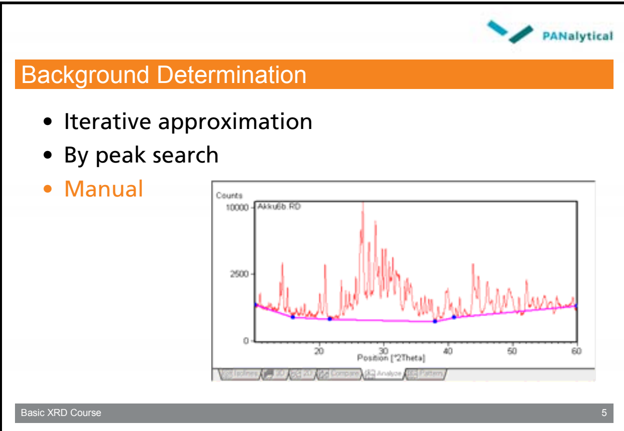






Identification with X'Pert HighScore: Search-match and Identification Background Information



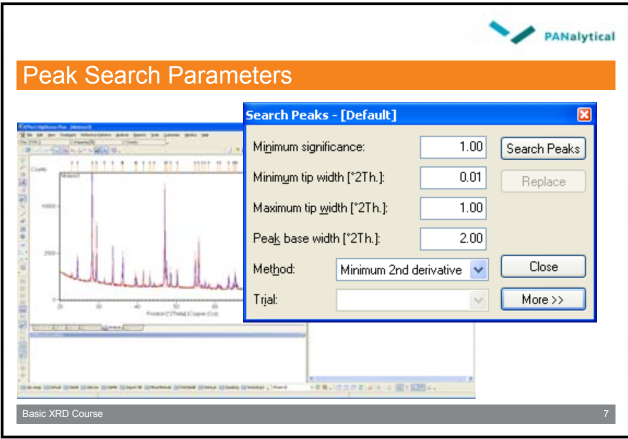


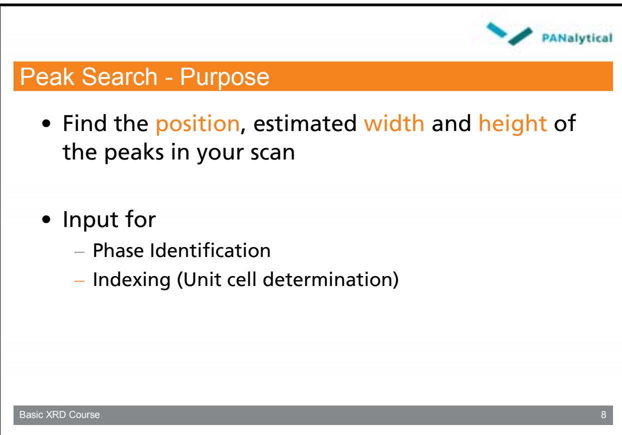
PANalytical

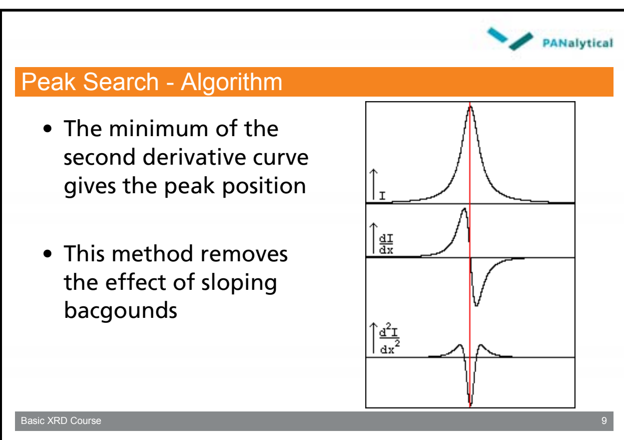
Pattern Treatments

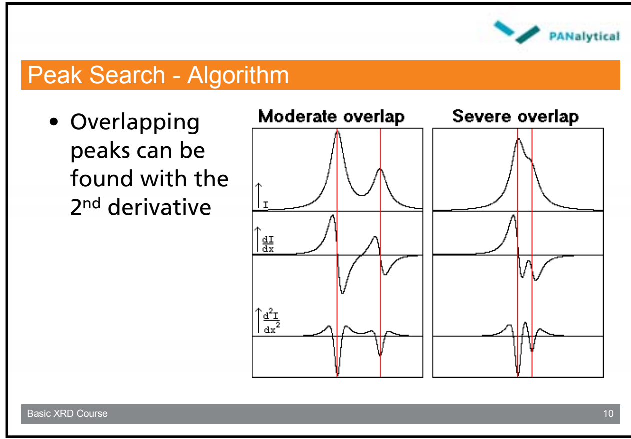
- Data reduction functions
  - *Background determination*
  - *Peak search*
  - *Profile fitting*
  - *$K\alpha_2$ stripping*
  - *Smoothing*
- Correction functions
  - *Divergence slit*
  - *....*
- Edit data

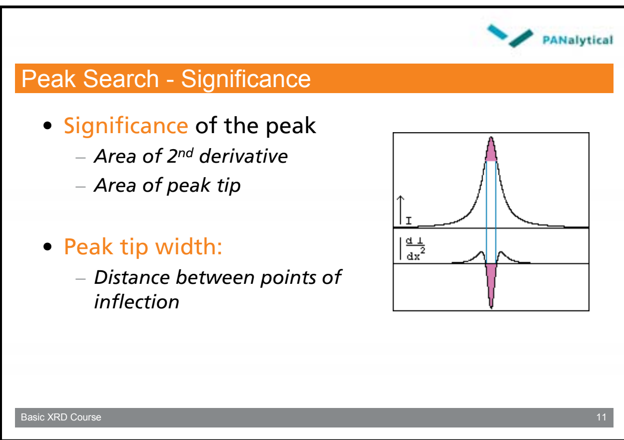
Basic XRD Course 6

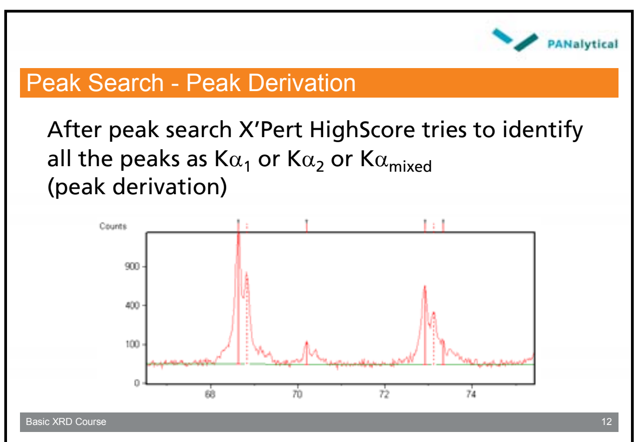

PANalytical
Peak Search Parameters
Search Peaks - [Default]
Minimum significance: 1.00
Minimum tip width [°2Th.]: 0.01
Maximum tip width [°2Th.]: 1.00
Peak base width [°2Th.]: 2.00
Method: Minimum 2nd derivative
Trial:
Search Peaks
Replace
Close
More >>
Basic XRD Course
7

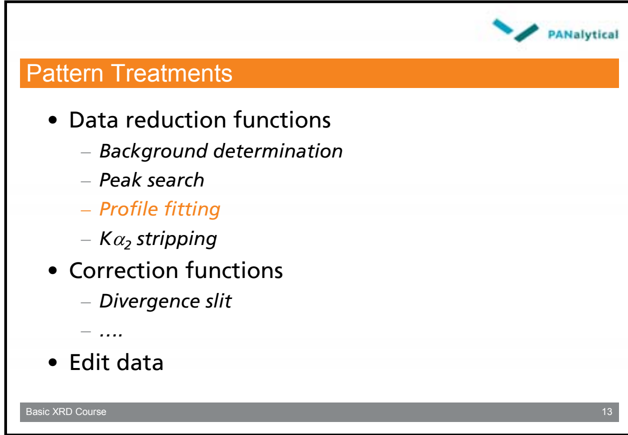

PANalytical
Peak Search - Purpose
• Find the position, estimated width and height of the peaks in your scan
• Input for
– Phase Identification
– Indexing (Unit cell determination)
Basic XRD Course
8

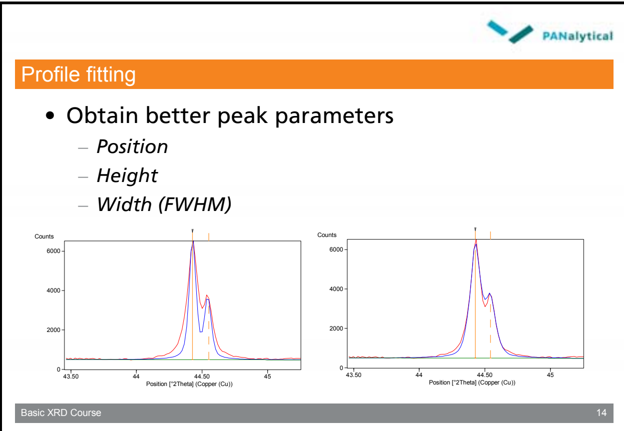

PANalytical
Peak Search - Algorithm
• The minimum of the second derivative curve gives the peak position
• This method removes the effect of sloping bacgounds
I
dI/dx
d²I/dx²
Basic XRD Course
9

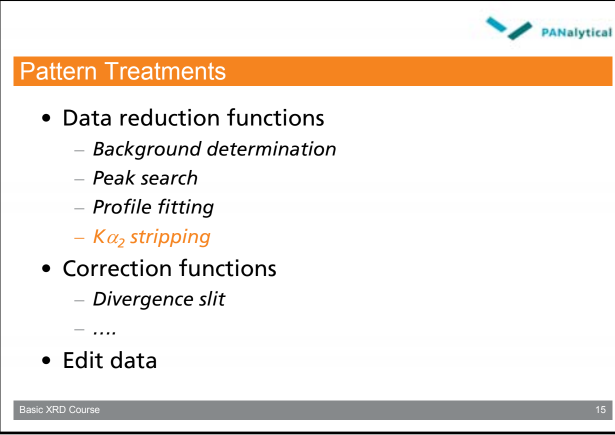

PANalytical
Peak Search - Algorithm
Overlapping peaks can be found with the 2nd derivative
Moderate overlap
Severe overlap
Basic XRD Course
10

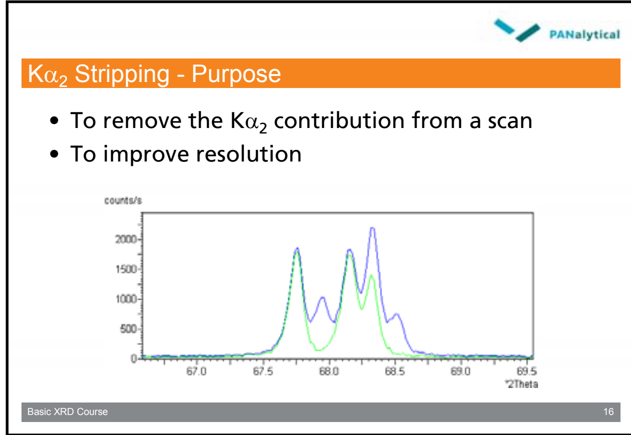

PANalytical
Peak Search - Significance
Significance of the peak
Area of 2nd derivative
Area of peak tip
Peak tip width:
Distance between points of inflection
Basic XRD Course
11

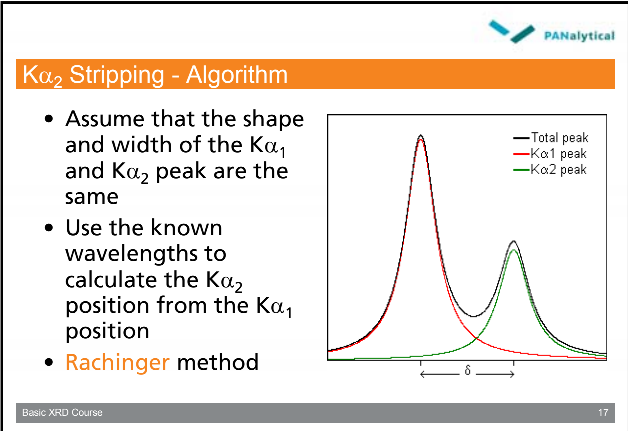

PANalytical
Peak Search - Peak Derivation
After peak search X'Pert HighScore tries to identify all the peaks as Kα1 or Kα2 or Kαmixed (peak derivation)
Counts
900
400
100
0
68
70
72
74
Basic XRD Course
12

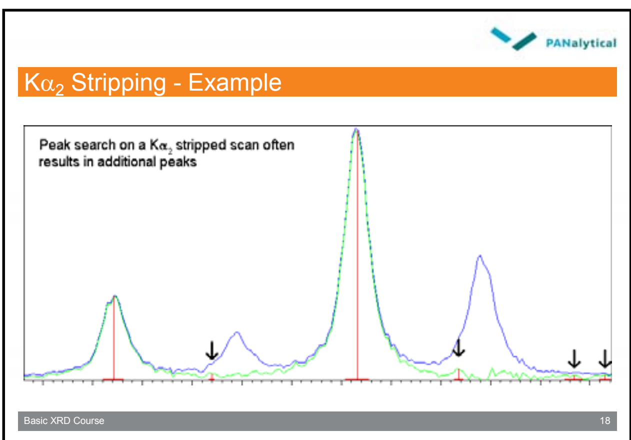

PANalytical
Pattern Treatments
• Data reduction functions
– Background determination
– Peak search
– Profile fitting
– Kα2 stripping
• Correction functions
– Divergence slit
– ....
• Edit data
Basic XRD Course
13


PANalytical
Profile fitting
• Obtain better peak parameters
– Position
– Height
– Width (FWHM)
Counts
Position [°2Theta] (Copper (Cu))
Basic XRD Course
14


PANalytical
Pattern Treatments
• Data reduction functions
– Background determination
– Peak search
– Profile fitting
– Kα2 stripping
• Correction functions
– Divergence slit
– ....
• Edit data
Basic XRD Course
15


PANalytical
Kα2 Stripping - Purpose
To remove the Kα2 contribution from a scan
To improve resolution
counts/s
2000
1500
1000
500
0
67.0
67.5
68.0
68.5
69.0
69.5
°2Theta
Basic XRD Course
16


PANalytical
Kα2 Stripping - Algorithm
Assume that the shape and width of the Kα1 and Kα2 peak are the same
Use the known wavelengths to calculate the Kα2 position from the Kα1 position
Rachinger method
Total peak
Kα1 peak
Kα2 peak
δ
Basic XRD Course
17


PANalytical
Kα2 Stripping - Example
Peak search on a Kα2 stripped scan often results in additional peaks
Basic XRD Course
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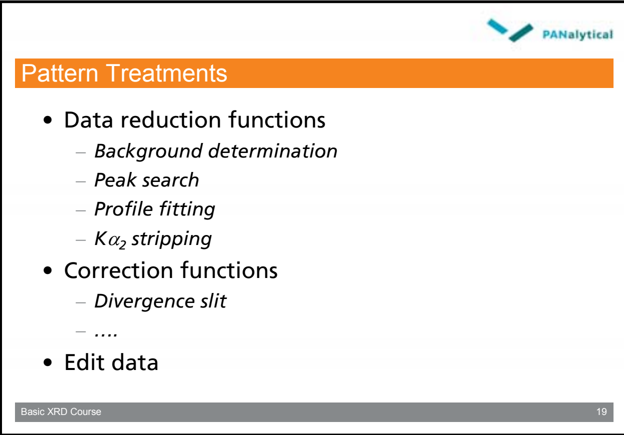
PANalytical
Pattern Treatments
Data reduction functions
Background determination
Peak search
Profile fitting
$K\alpha_2$ stripping
Correction functions
Divergence slit
....
Edit data
Basic XRD Course
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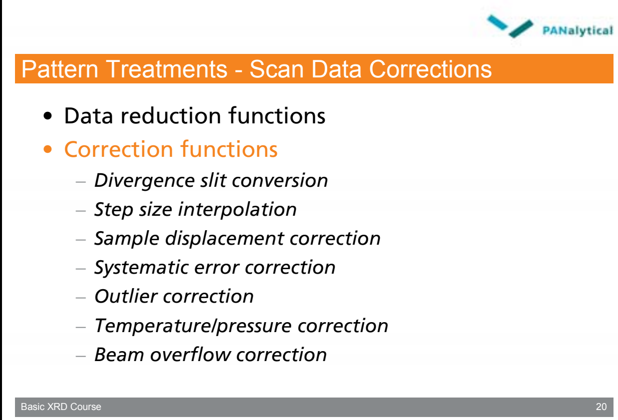
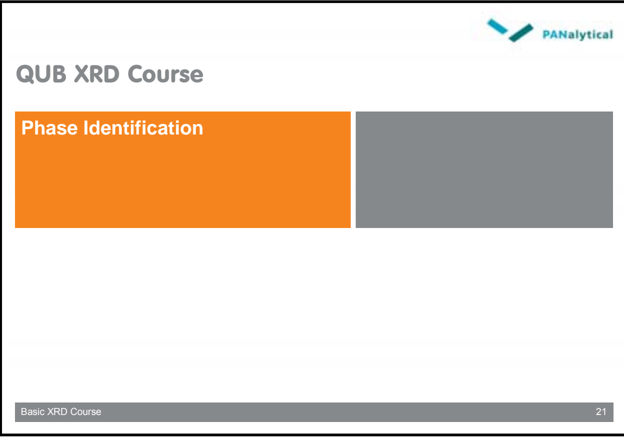

PANalytical
Pattern Treatments - Scan Data Corrections
Data reduction functions
Correction functions
Divergence slit conversion
Step size interpolation
Sample displacement correction
Systematic error correction
Outlier correction
Temperature/pressure correction
Beam overflow correction
Basic XRD Course
20


PANalytical
QUB XRD Course
Phase Identification
Basic XRD Course
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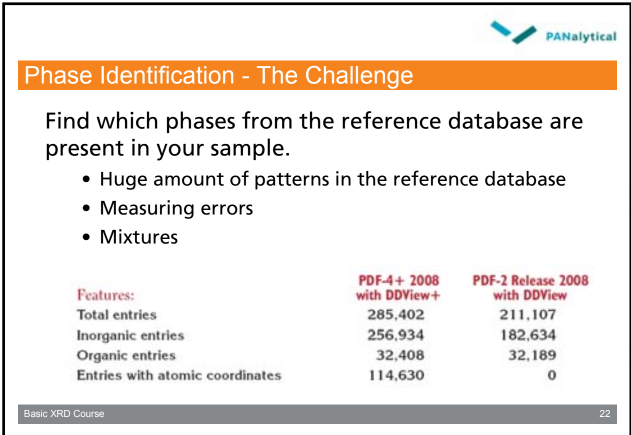

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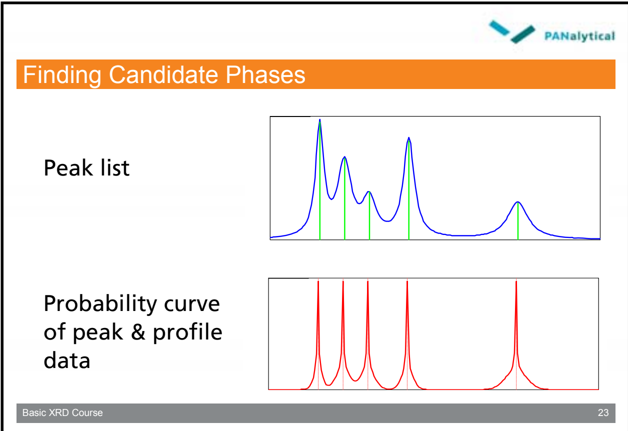
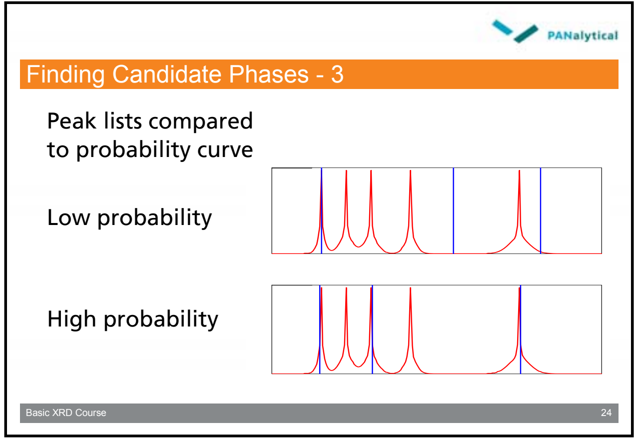
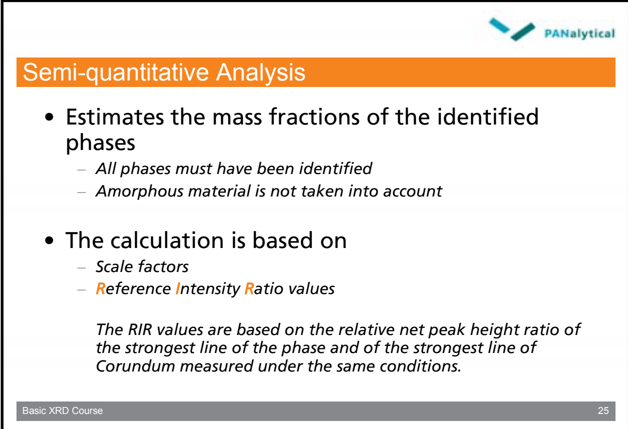
Total entries	285,402	211,107
Inorganic entries	256,934	182,634
Organic entries	32,408	32,189
Entries with atomic coordinates	114,630	0






PANalytical
Semi-quantitative Analysis
• Estimates the mass fractions of the identified phases
– All phases must have been identified
– Amorphous material is not taken into account
• The calculation is based on
– Scale factors
– Reference Intensity Ratio values
The RIR values are based on the relative net peak height ratio of the strongest line of the phase and of the strongest line of Corundum measured under the same conditions.
Basic XRD Course
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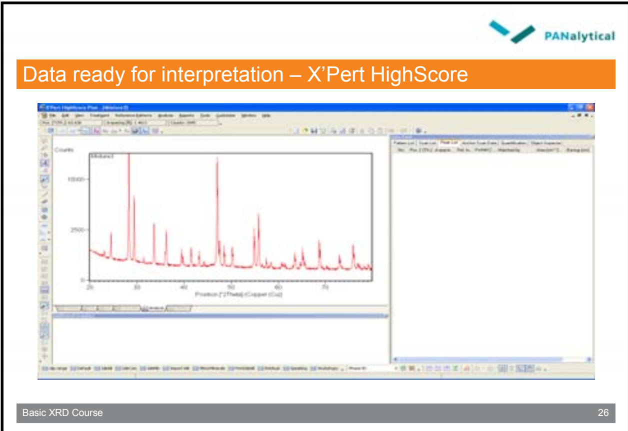
PANalytical
Data ready for interpretation – X'Pert HighScore
Basic XRD Course
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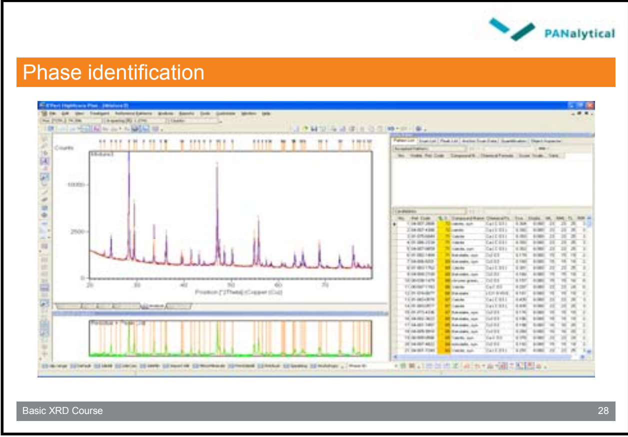
PANalytical
Pattern Treatment
Basic XRD Course
27


PANalytical
Phase identification
Basic XRD Course
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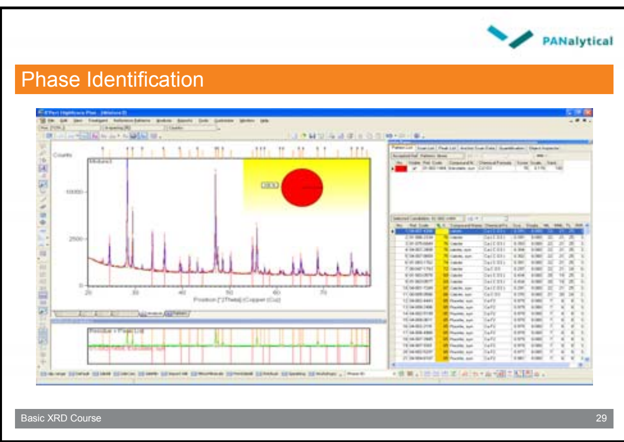
PANalytical
Phase Identification
Basic XRD Course
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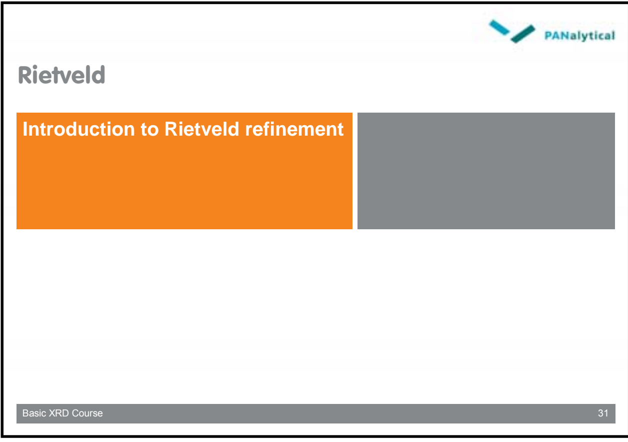
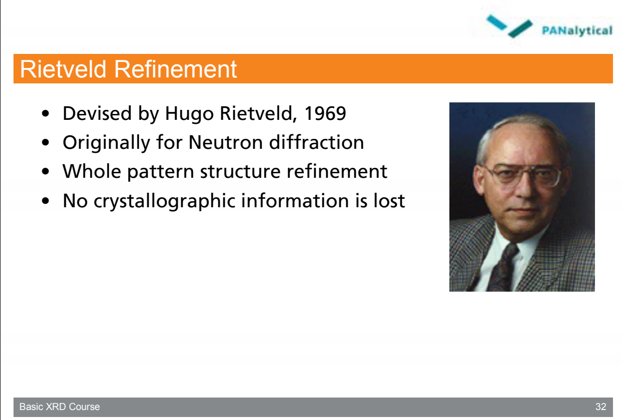
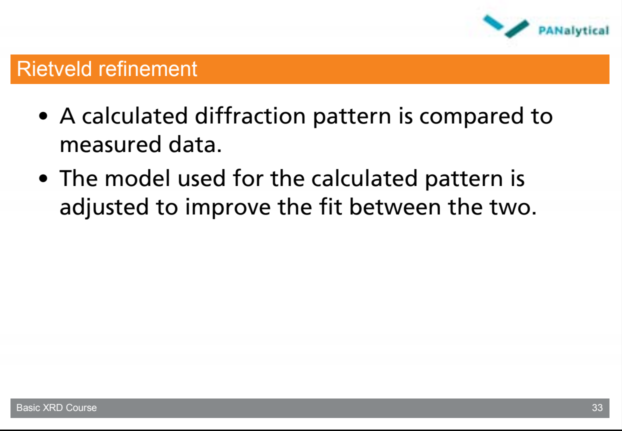
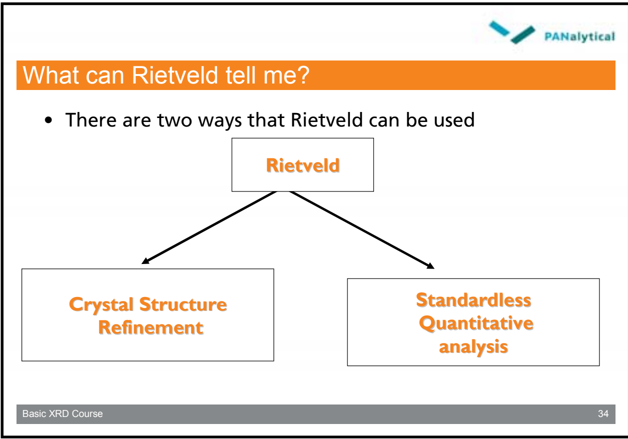
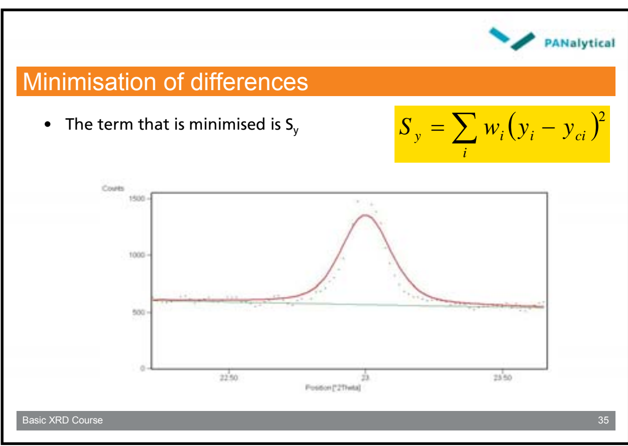
PANalytical
Phase Identification
Basic XRD Course
30

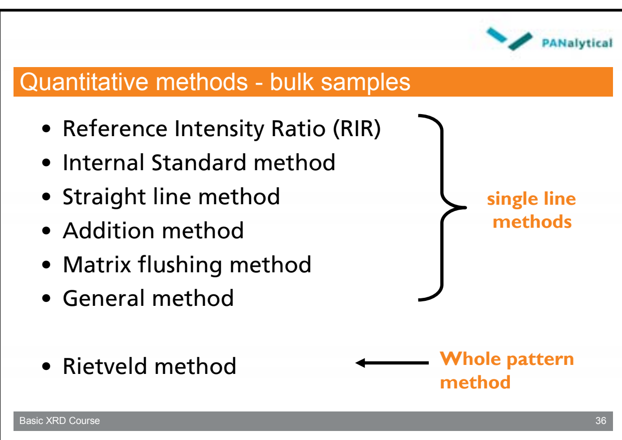

PANalytical
Rietveld
Introduction to Rietveld refinement
Basic XRD Course
31

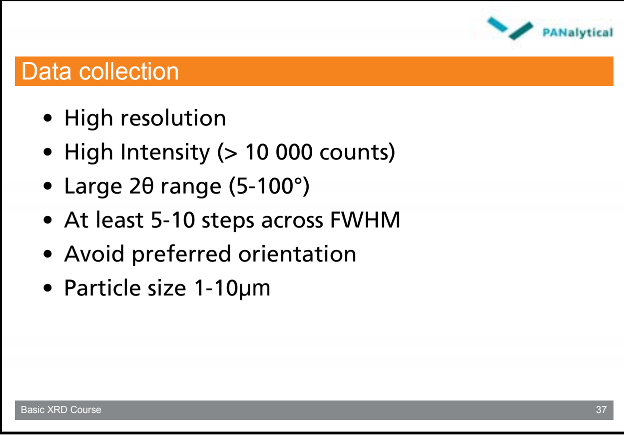

PANalytical
Rietveld Refinement
Devised by Hugo Rietveld, 1969
Originally for Neutron diffraction
Whole pattern structure refinement
No crystallographic information is lost
Basic XRD Course
32

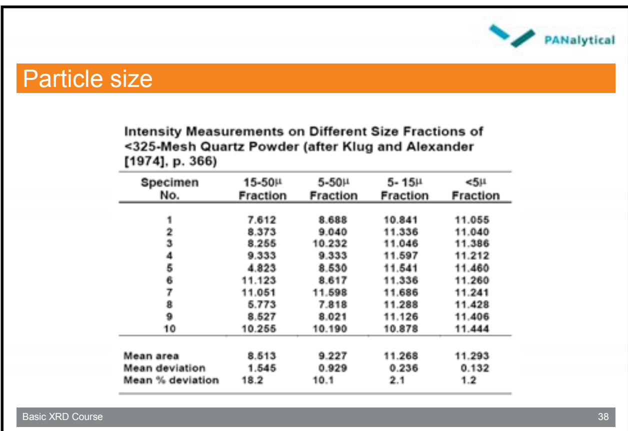

PANalytical
Rietveld refinement
A calculated diffraction pattern is compared to measured data.
The model used for the calculated pattern is adjusted to improve the fit between the two.
Basic XRD Course
33


PANalytical
What can Rietveld tell me?
There are two ways that Rietveld can be used
Rietveld
Crystal Structure Refinement
Standardless Quantitative analysis
Basic XRD Course
34


PANalytical
Minimisation of differences
The term that is minimised is S_y
$S_y = \sum_i w_i (y_i - y_{ci})^2$
Basic XRD Course
35


PANalytical
Quantitative methods - bulk samples
Reference Intensity Ratio (RIR)
Internal Standard method
Straight line method
Addition method
Matrix flushing method
General method
single line methods
Rietveld method
Whole pattern method
Basic XRD Course
36





Intensity Measurements on Different Size Fractions of <325-Mesh Quartz Powder (after Klug and Alexander [1974], p. 366)

Specimen No.	15-50µ Fraction	5-50µ Fraction	5- 15µ Fraction	<5µ Fraction
1	7.612	8.688	10.841	11.055
2	8.373	9.040	11.336	11.040
3	8.255	10.232	11.046	11.386
4	9.333	9.333	11.597	11.212
5	4.823	8.530	11.541	11.460
6	11.123	8.617	11.336	11.260
7	11.051	11.598	11.686	11.241
8	5.773	7.818	11.288	11.428
9	8.527	8.021	11.126	11.406
10	10.255	10.190	10.878	11.444
Mean area	8.513	9.227	11.268	11.293
Mean deviation	1.545	0.929	0.236	0.132
Mean % deviation	18.2	10.1	2.1	1.2

PANalytical

Calculated intensity

$$y_{ci} = s \sum_K L_K |F_K|^2 \phi(2\theta_i - 2\theta_K) P_K A + y_{bi}$$

S = Scale factor

K represents the Miller indices

L_K= Lorenz polarisation and multiplicity factors

Φ is the reflection profile function

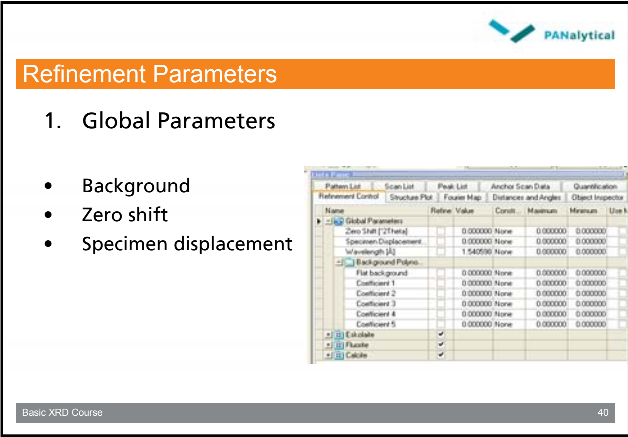
P_K is the preferred orientation function

A is the absorption factor

F_K is the structure factor of the Kth Bragg reflection

Y_{bi} is the background intensity of the *i*th step

Basic XRD Course 39


PANalytical
Refinement Parameters
1. Global Parameters
Background
Zero shift
Specimen displacement
Basic XRD Course
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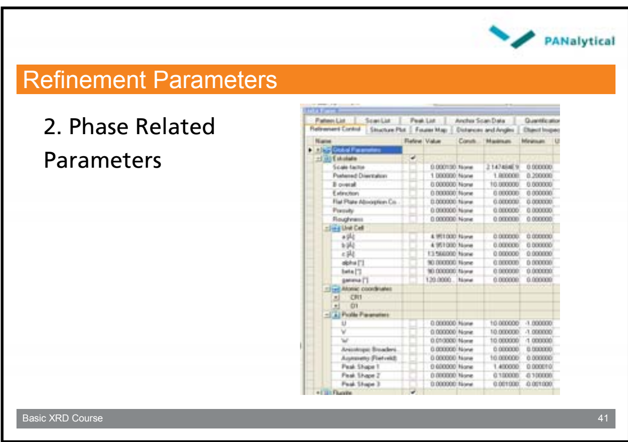
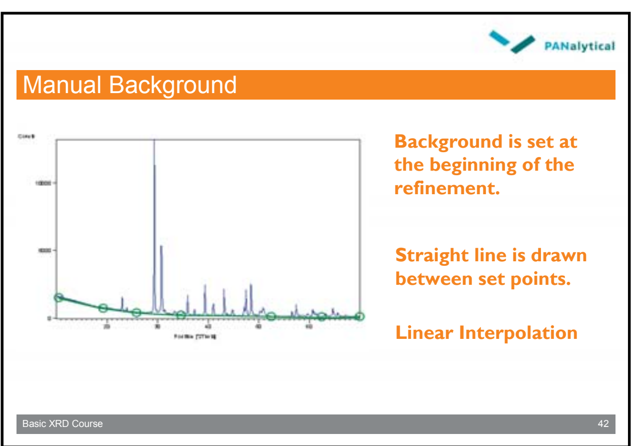
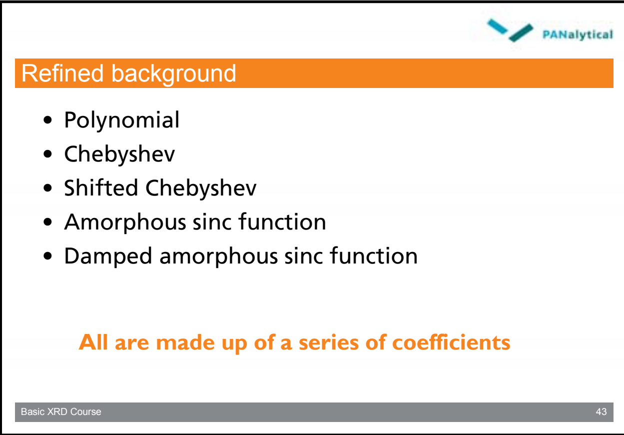

PANalytical
Refinement Parameters
2. Phase Related Parameters
Basic XRD Course
41


PANalytical
Manual Background
Background is set at the beginning of the refinement.
Straight line is drawn between set points.
Linear Interpolation
Basic XRD Course
42


PANalytical
Refined background
Polynomial
Chebyshev
Shifted Chebyshev
Amorphous sinc function
Damped amorphous sinc function
All are made up of a series of coefficients
Basic XRD Course
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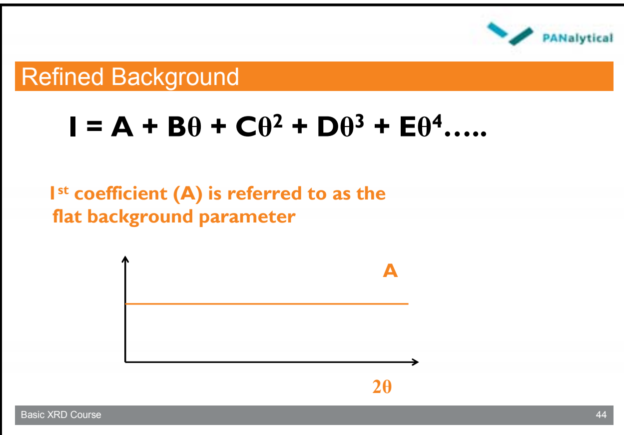
PANalytical
Refined Background
I = A + Bθ + Cθ2 + Dθ3 + Eθ4…..
1st coefficient (A) is referred to as the
flat background parameter
A
2θ
Basic XRD Course
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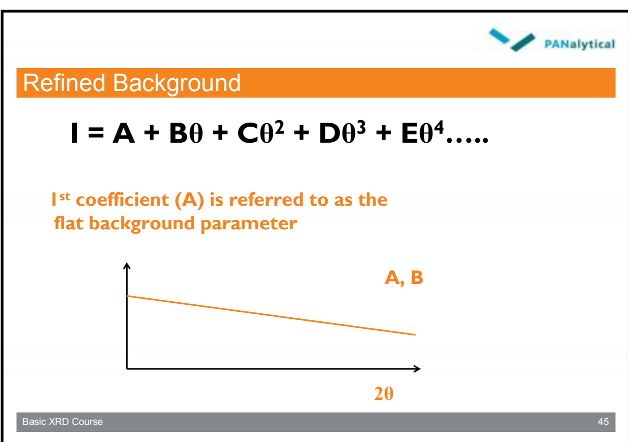
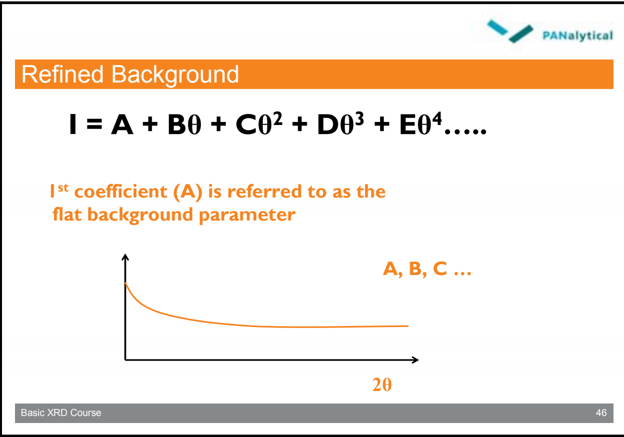
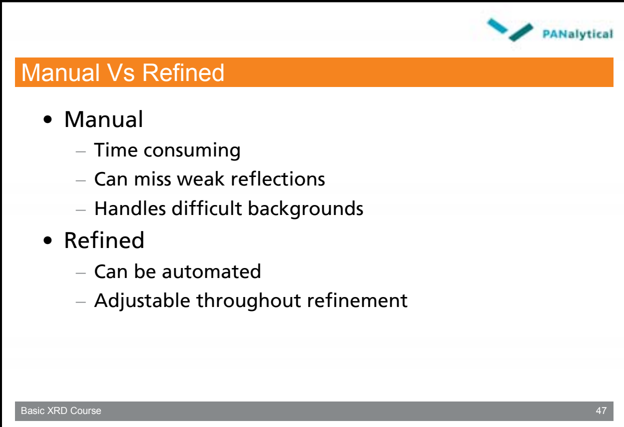
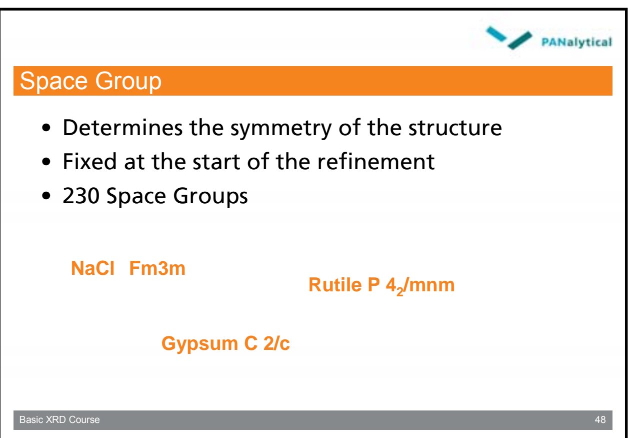
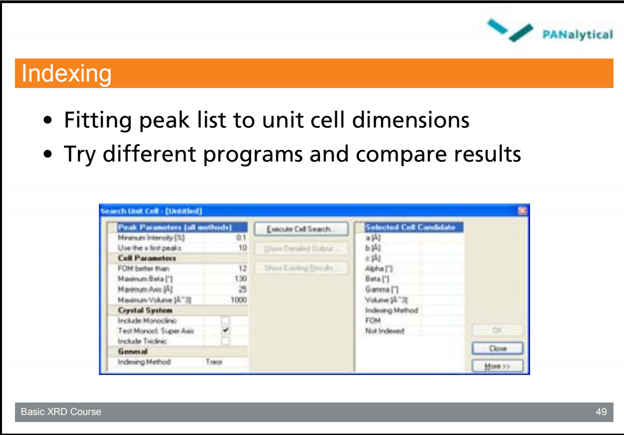

PANalytical
Refined Background
I = A + Bθ + Cθ2 + Dθ3 + Eθ4…..
1st coefficient (A) is referred to as the
flat background parameter
A, B
2θ
Basic XRD Course
45

Identification with X'Pert HighScore: Search-match and Identification Background Information








PANalytical
Indexing
Fitting peak list to unit cell dimensions
Try different programs and compare results
Basic XRD Course
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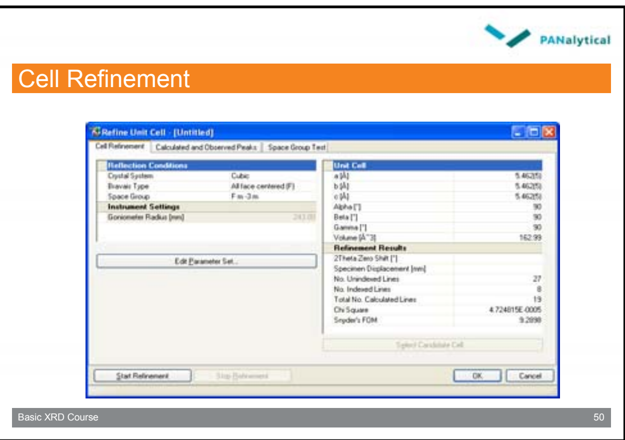
PANalytical
Cell Refinement
Basic XRD Course
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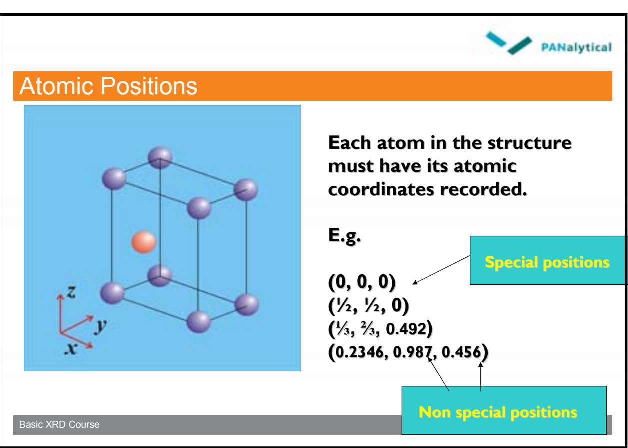
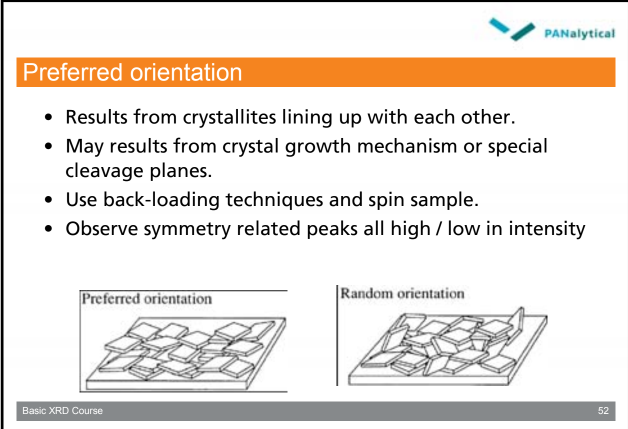

PANalytical
Atomic Positions
Each atom in the structure must have its atomic coordinates recorded.
E.g.
(0, 0, 0)
(½, ½, 0)
(⅓, ⅔, 0.492)
(0.2346, 0.987, 0.456)
Special positions
Non special positions
Basic XRD Course


PANalytical
Preferred orientation
• Results from crystallites lining up with each other.
• May results from crystal growth mechanism or special cleavage planes.
• Use back-loading techniques and spin sample.
• Observe symmetry related peaks all high / low in intensity
Preferred orientation
Random orientation
Basic XRD Course
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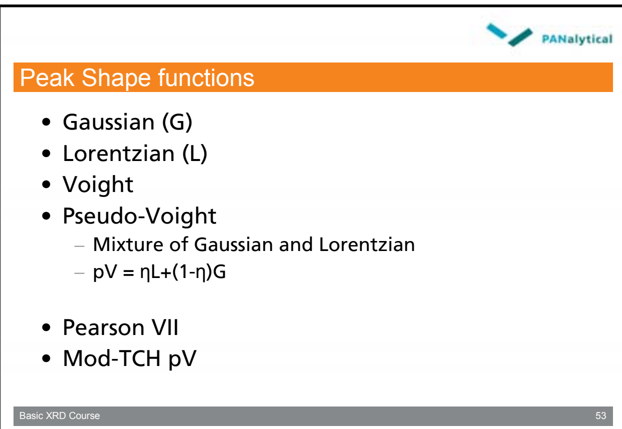
PANalytical
Peak Shape functions
• Gaussian (G)
• Lorentzian (L)
• Voight
• Pseudo-Voight
– Mixture of Gaussian and Lorentzian
– pV = ηL+(1-η)G
• Pearson VII
• Mod-TCH pV
Basic XRD Course
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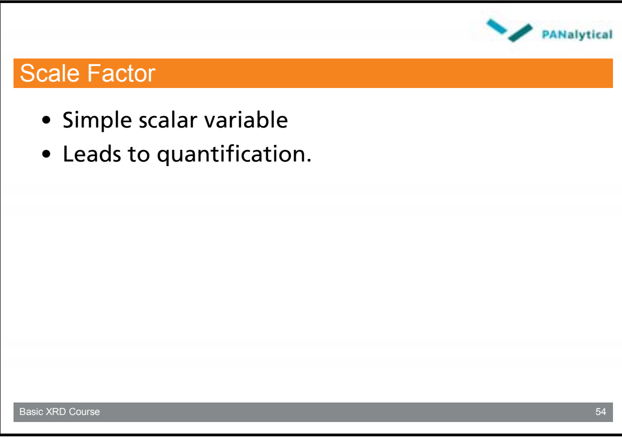
PANalytical
Scale Factor
• Simple scalar variable
• Leads to quantification.
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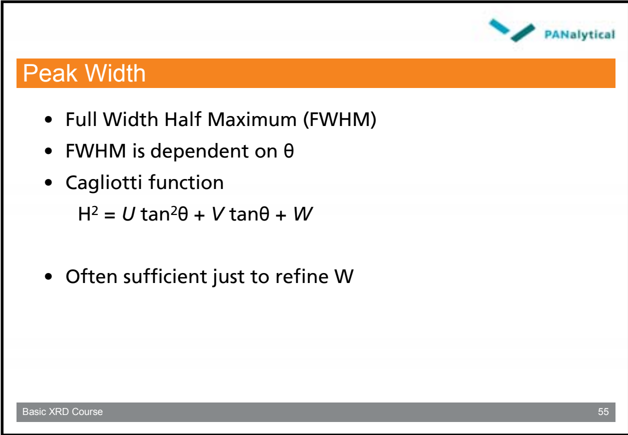
PANalytical
Peak Width
Full Width Half Maximum (FWHM)
FWHM is dependent on θ
Cagliotti function
H² = U tan²θ + V tanθ + W
Often sufficient just to refine W
Basic XRD Course
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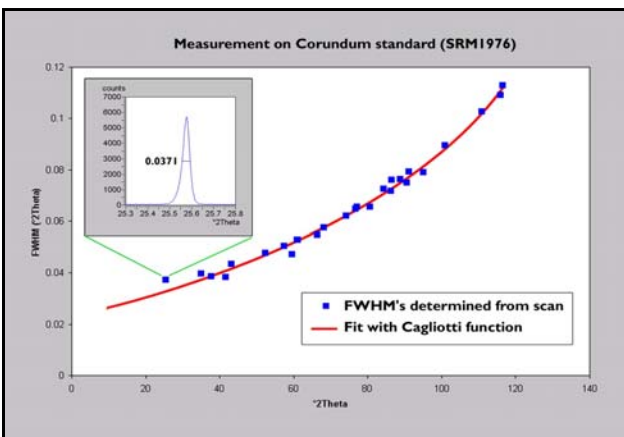
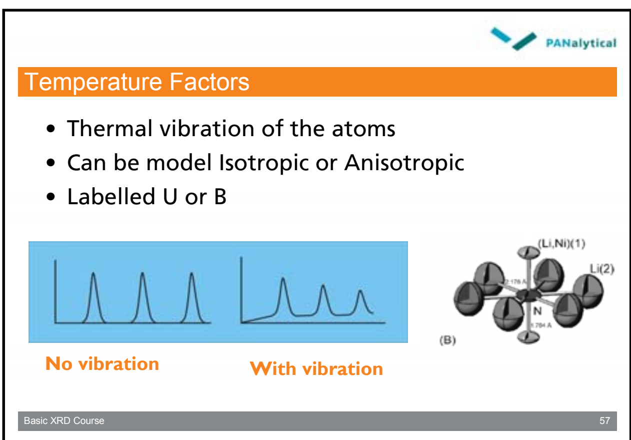

Measurement on Corundum standard (SRM1976)
FWHM (°2Theta)
°2Theta
0.0371
FWHM's determined from scan
Fit with Cagliotti function


PANalytical
Temperature Factors
Thermal vibration of the atoms
Can be model Isotropic or Anisotropic
Labelled U or B
No vibration
With vibration
(Li,Ni)(1)
Li(2)
N
(B)
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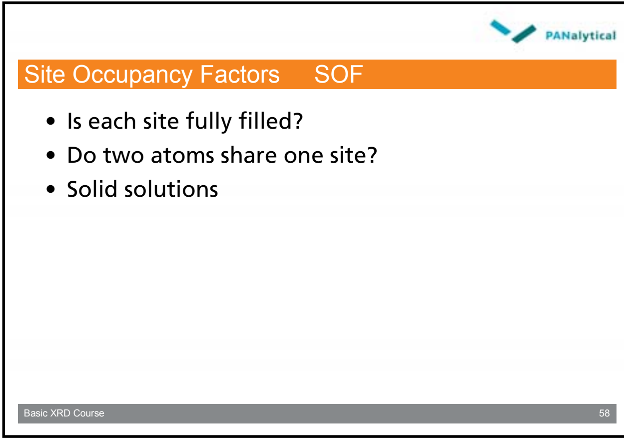
PANalytical
Site Occupancy Factors SOF
Is each site fully filled?
Do two atoms share one site?
Solid solutions
Basic XRD Course
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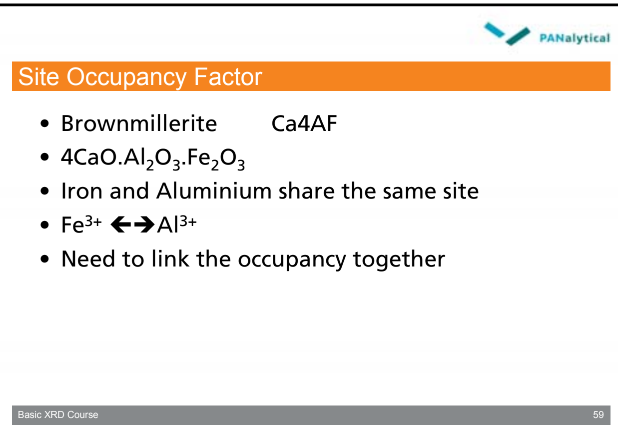
PANalytical
Site Occupancy Factor
Brownmillerite Ca4AF
$4CaO.Al_2O_3.Fe_2O_3$
Iron and Aluminium share the same site
$Fe^{3+} \leftrightarrow Al^{3+}$
Need to link the occupancy together
Basic XRD Course
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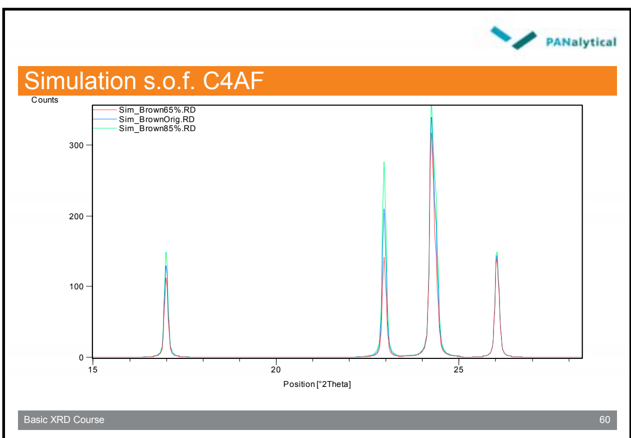
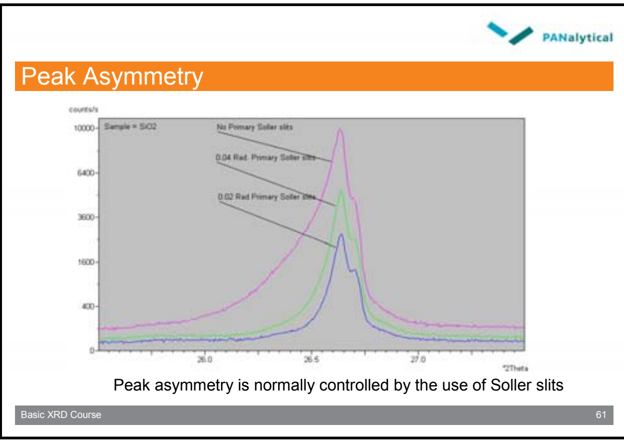

PANalytical
Simulation s.o.f. C4AF
Counts
Sim_Brown65%.RD
Sim_BrownOrig.RD
Sim_Brown85%.RD
300
200
100
0
15
20
25
Position [°2Theta]
Basic XRD Course
60


PANalytical
Peak Asymmetry
Peak asymmetry is normally controlled by the use of Soller slits
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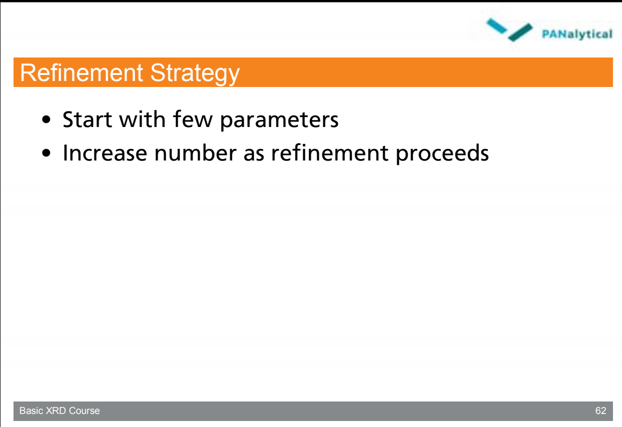
PANalytical
Refinement Strategy
• Start with few parameters
• Increase number as refinement proceeds
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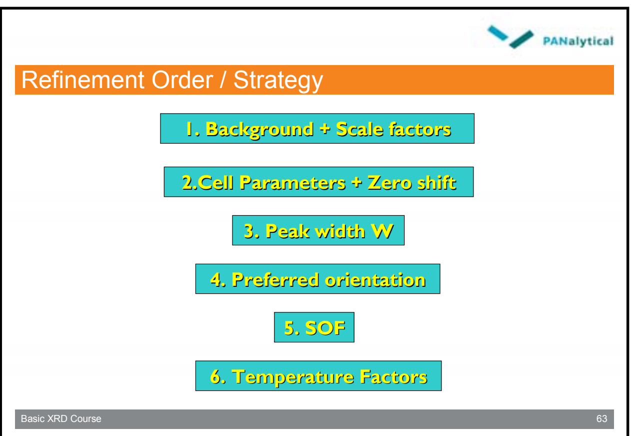
PANalytical
Refinement Order / Strategy
1. Background + Scale factors
2.Cell Parameters + Zero shift
3. Peak width W
4. Preferred orientation
5. SOF
6. Temperature Factors
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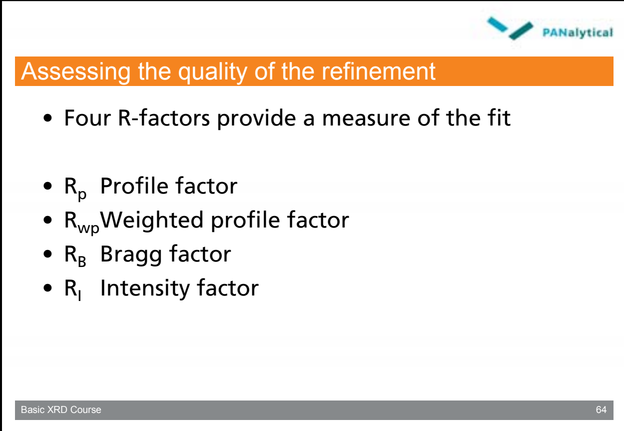
63


PANalytical
Assessing the quality of the refinement
• Four R-factors provide a measure of the fit
• R_p Profile factor
• R_{wp} Weighted profile factor
• R_B Bragg factor
• R_I Intensity factor
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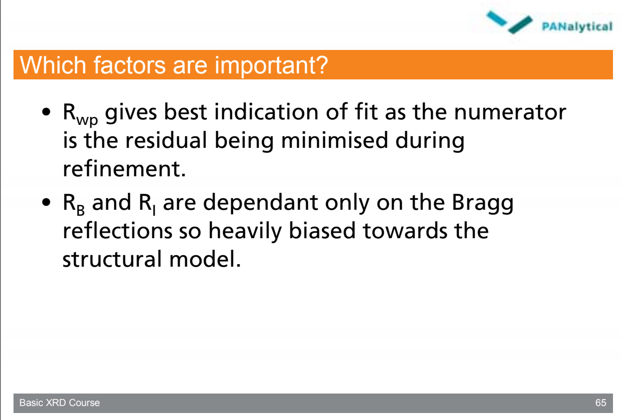
PANalytical
Which factors are important?
• R_{wp} gives best indication of fit as the numerator is the residual being minimised during refinement.
• R_B and R_I are dependant only on the Bragg reflections so heavily biased towards the structural model.
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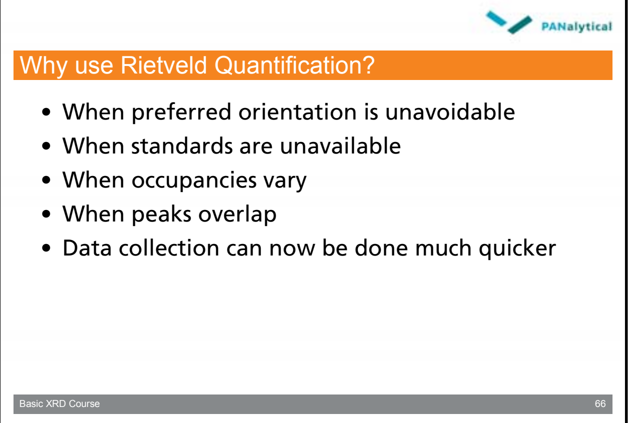
PANalytical
Why use Rietveld Quantification?
• When preferred orientation is unavoidable
• When standards are unavailable
• When occupancies vary
• When peaks overlap
• Data collection can now be done much quicker
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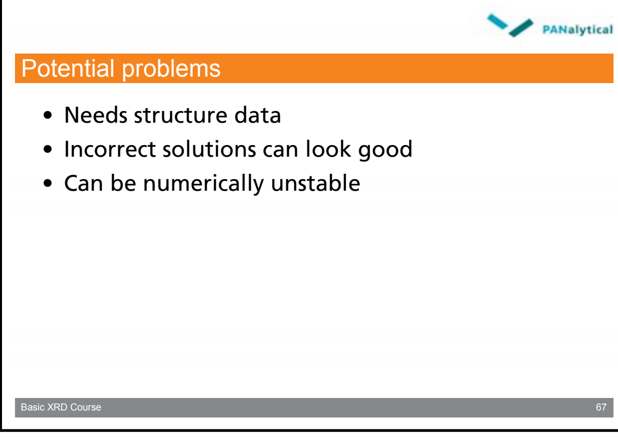
PANalytical
Potential problems
• Needs structure data
• Incorrect solutions can look good
• Can be numerically unstable
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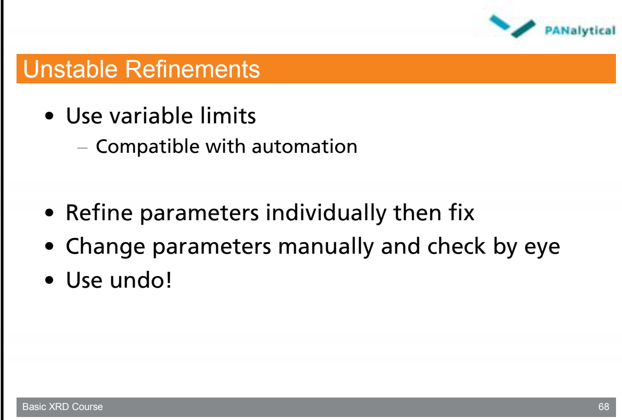
PANalytical
Unstable Refinements
• Use variable limits
– Compatible with automation
• Refine parameters individually then fix
• Change parameters manually and check by eye
• Use undo!
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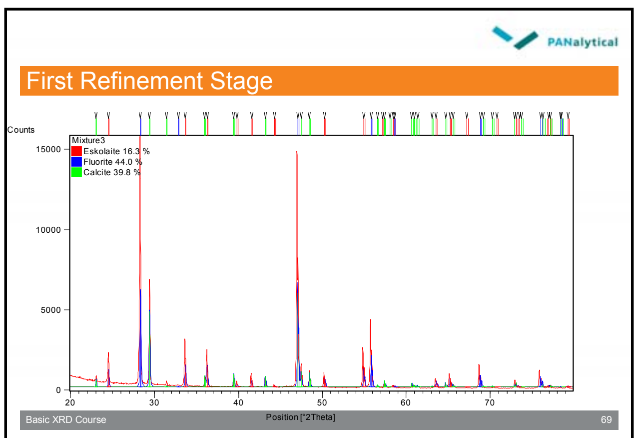
PANalytical
First Refinement Stage
Counts
Mixture3
Eskolaite 16.3 %
Fluorite 44.0 %
Calcite 39.8 %
15000
10000
5000
0
20
30
40
50
60
70
Position [°2Theta]
Basic XRD Course
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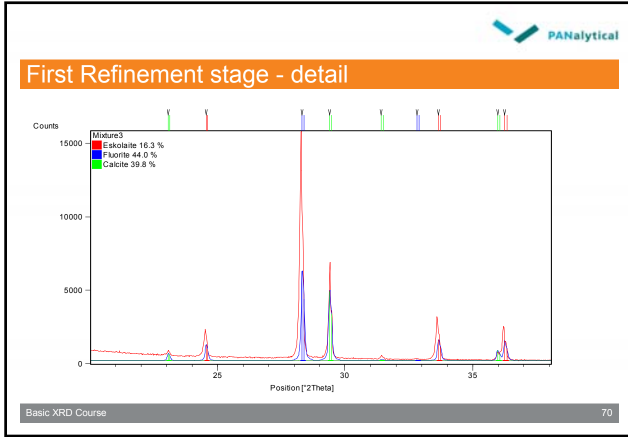
PANalytical
First Refinement stage - detail
Counts
Mixture3
Eskolaite 16.3 %
Fluorite 44.0 %
Calcite 39.8 %
15000
10000
5000
0
25
30
35
Position [°2Theta]
Basic XRD Course
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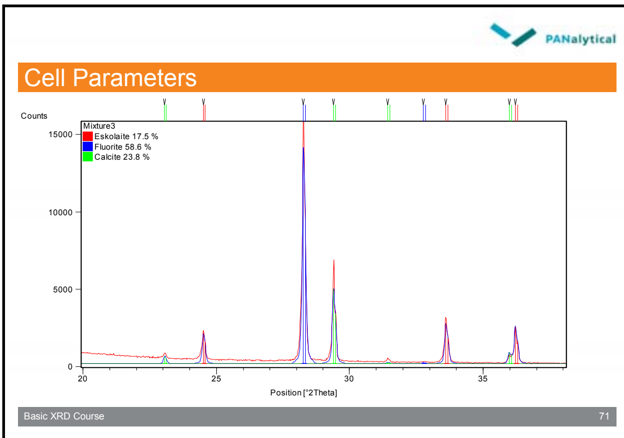
PANalytical
Cell Parameters
Counts
Mixture3
Eskolaite 17.5 %
Fluorite 58.6 %
Calcite 23.8 %
15000
10000
5000
0
20
25
30
35
Position [°2Theta]
Basic XRD Course
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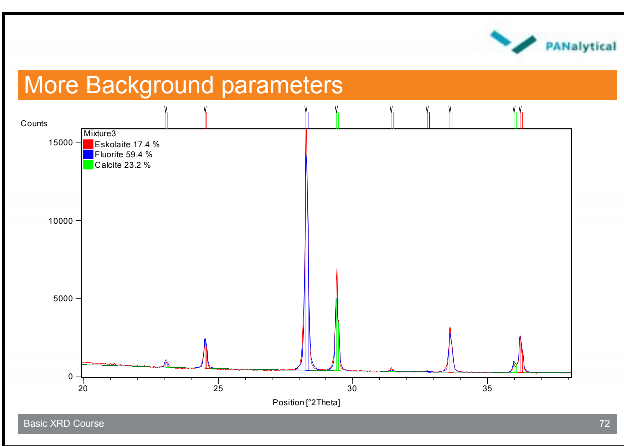
PANalytical
More Background parameters
Counts
Mixture3
Eskolaite 17.4 %
Fluorite 59.4 %
Calcite 23.2 %
15000
10000
5000
0
20
25
30
35
Position [°2Theta]
Basic XRD Course
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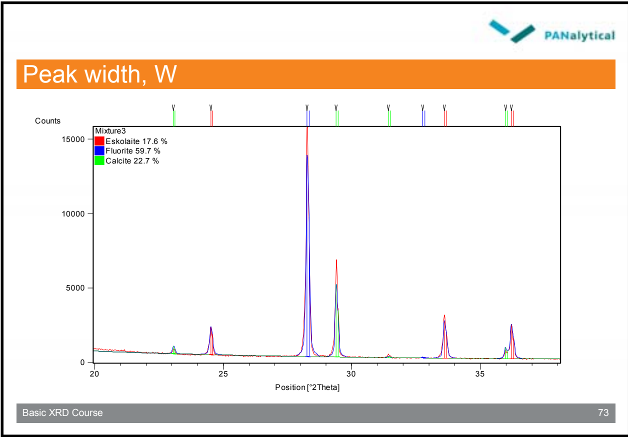
PANalytical
Peak width, W
Counts
15000
10000
5000
0
Mixture3
Eskolaite 17.6 %
Fluorite 59.7 %
Calcite 22.7 %
20
25
30
35
Position [°2Theta]
Basic XRD Course
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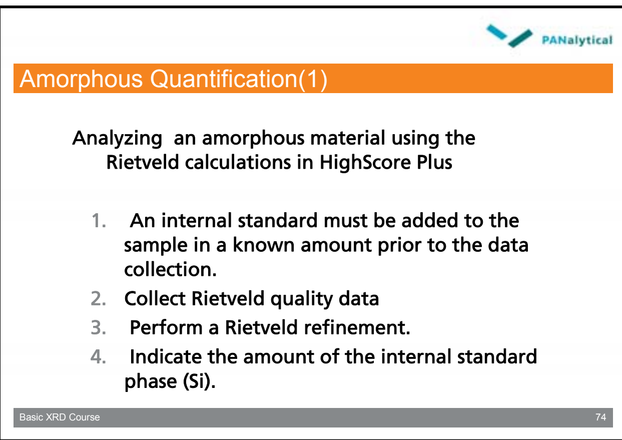
PANalytical
Amorphous Quantification(1)
Analyzing an amorphous material using the Rietveld calculations in HighScore Plus
1. An internal standard must be added to the sample in a known amount prior to the data collection.
2. Collect Rietveld quality data
3. Perform a Rietveld refinement.
4. Indicate the amount of the internal standard phase (Si).
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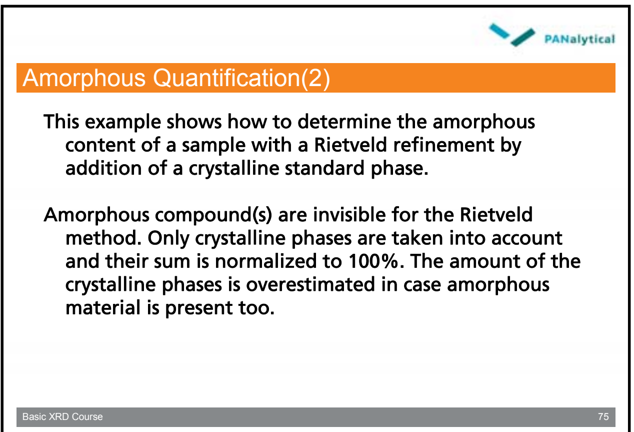
PANalytical
Amorphous Quantification(2)
This example shows how to determine the amorphous content of a sample with a Rietveld refinement by addition of a crystalline standard phase.
Amorphous compound(s) are invisible for the Rietveld method. Only crystalline phases are taken into account and their sum is normalized to 100%. The amount of the crystalline phases is overestimated in case amorphous material is present too.
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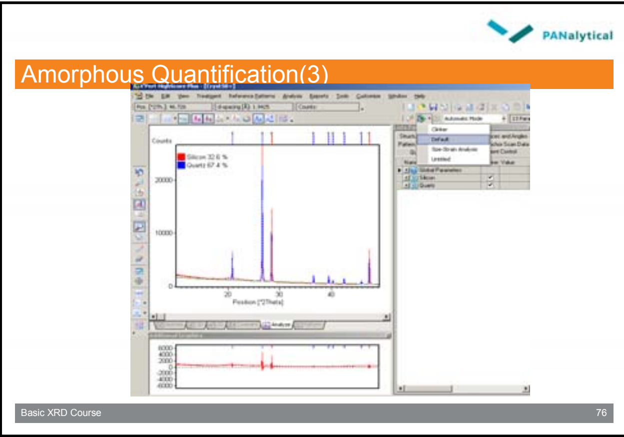
PANalytical
Amorphous Quantification(3)
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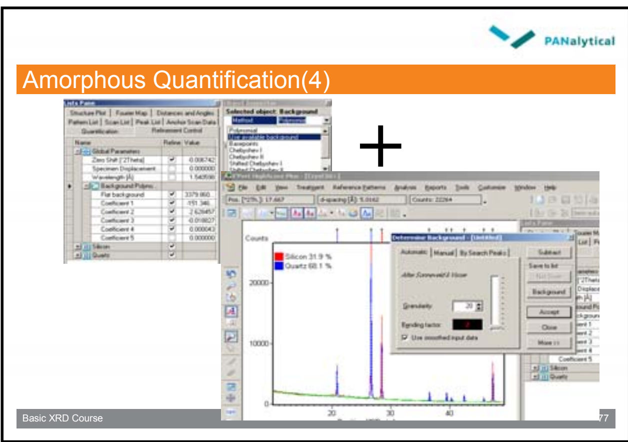
PANalytical
Amorphous Quantification(4)
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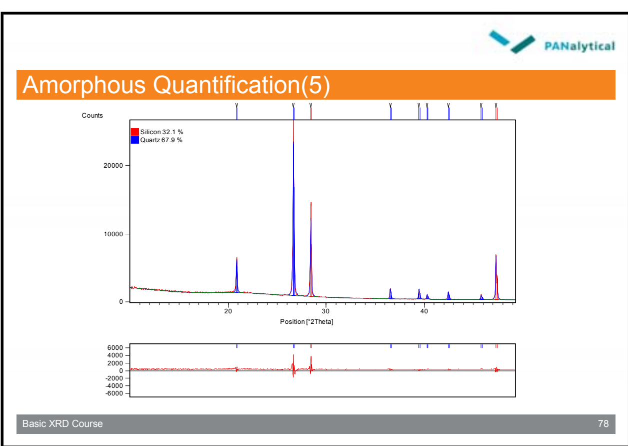
PANalytical
Amorphous Quantification(5)
Counts
Silicon 32.1 %
Quartz 67.9 %
Position [°2Theta]
Basic XRD Course
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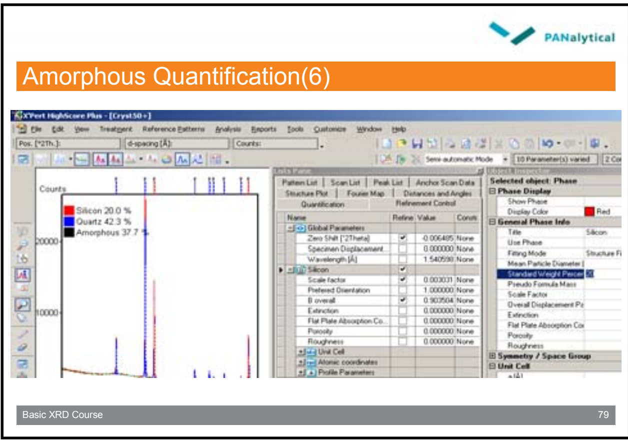
PANalytical
Amorphous Quantification(6)
Silicon 20.0 %
Quartz 42.3 %
Amorphous 37.7 %
Basic XRD Course
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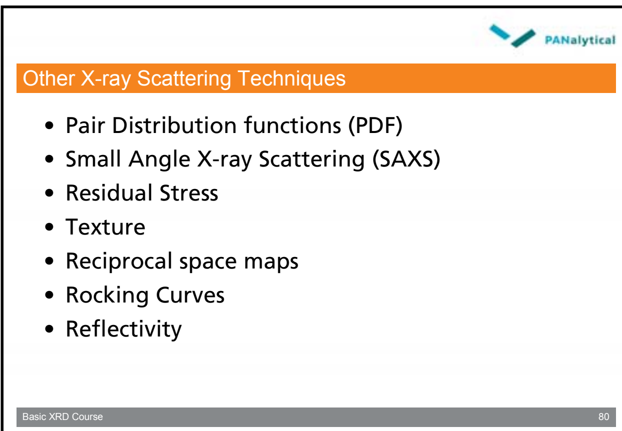
PANalytical
Other X-ray Scattering Techniques
• Pair Distribution functions (PDF)
• Small Angle X-ray Scattering (SAXS)
• Residual Stress
• Texture
• Reciprocal space maps
• Rocking Curves
• Reflectivity
Basic XRD Course
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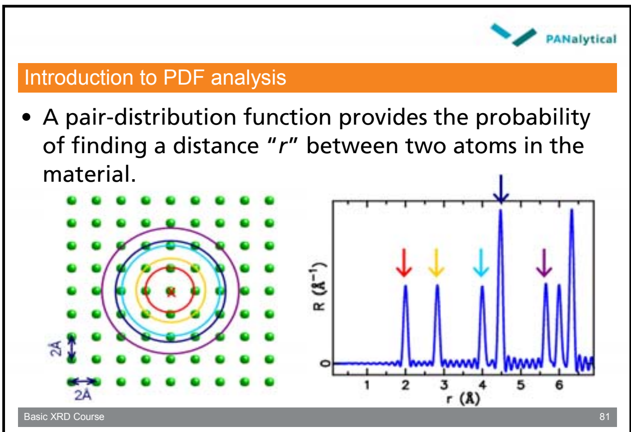
PANalytical
Introduction to PDF analysis
• A pair-distribution function provides the probability of finding a distance "r" between two atoms in the material.
2Å
2Å
R (Å⁻¹)
0
1 2 3 4 5 6
r (Å)
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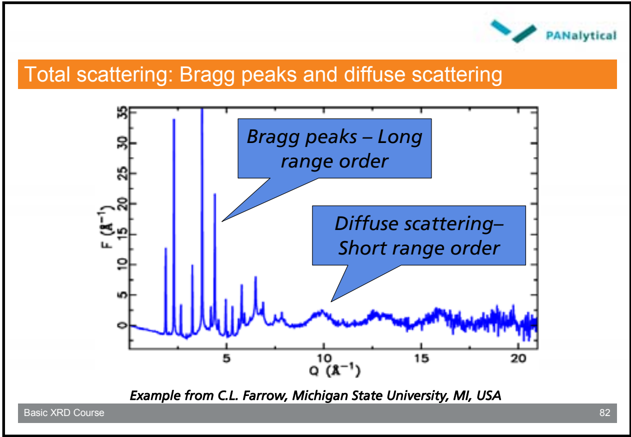
PANalytical
Total scattering: Bragg peaks and diffuse scattering
Bragg peaks – Long range order
Diffuse scattering– Short range order
F (Å⁻¹)
Q (Å⁻¹)
Example from C.L. Farrow, Michigan State University, MI, USA
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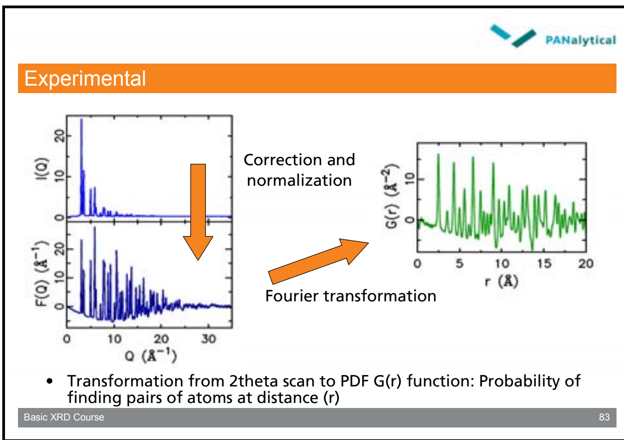
PANalytical
Experimental
I(Q)
F(Q) (Å⁻¹)
Q (Å⁻¹)
Correction and normalization
Fourier transformation
G(r) (Å⁻²)
r (Å)
Transformation from 2theta scan to PDF G(r) function: Probability of finding pairs of atoms at distance (r)
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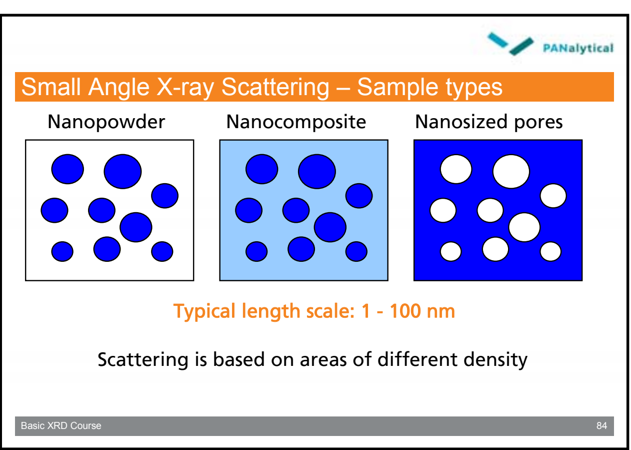
PANalytical
Small Angle X-ray Scattering – Sample types
Nanopowder
Nanocomposite
Nanosized pores
Typical length scale: 1 - 100 nm
Scattering is based on areas of different density
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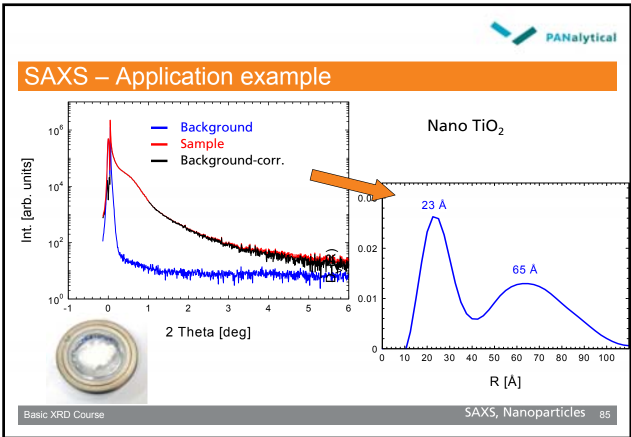
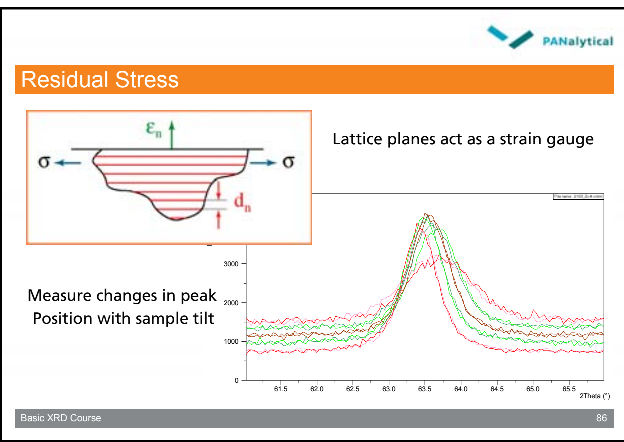


PANalytical
SAXS – Application example
Background
Sample
Background-corr.
Int. [arb. units]
2 Theta [deg]
Nano TiO_2
23 Å
65 Å
R [Å]
Basic XRD Course
SAXS, Nanoparticles
85



PANalytical
Residual Stress
Lattice planes act as a strain gauge
Measure changes in peak
Position with sample tilt
2Theta (°)
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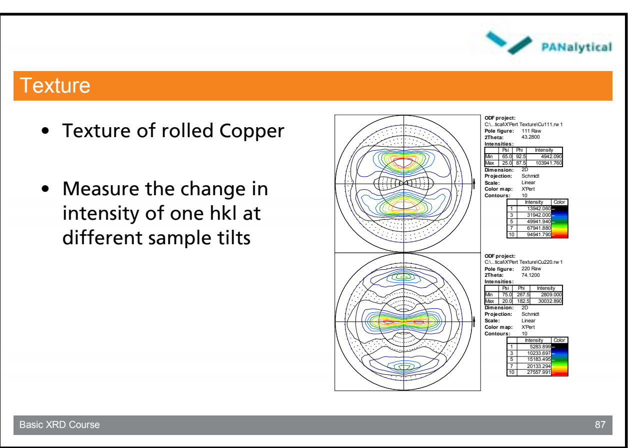

PANalytical
Texture
• Texture of rolled Copper
• Measure the change in intensity of one hkl at different sample tilts
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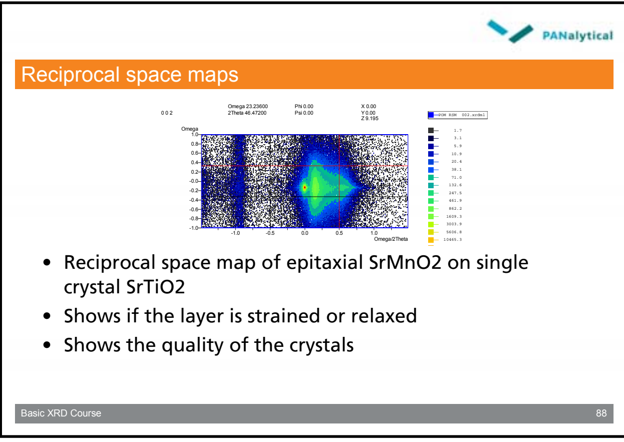
PANalytical
Reciprocal space maps
Reciprocal space map of epitaxial SrMnO2 on single crystal SrTiO2
Shows if the layer is strained or relaxed
Shows the quality of the crystals
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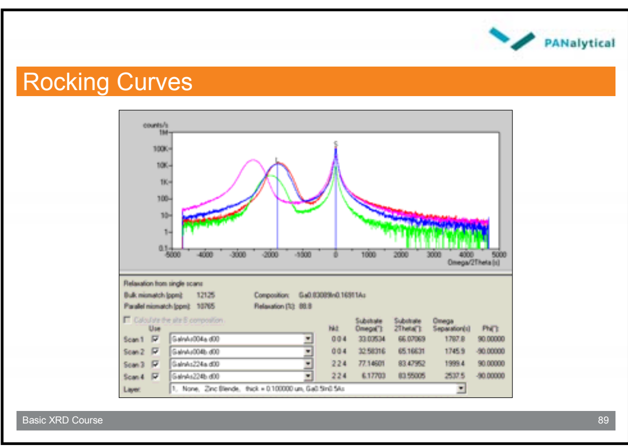
PANalytical
Rocking Curves
Basic XRD Course
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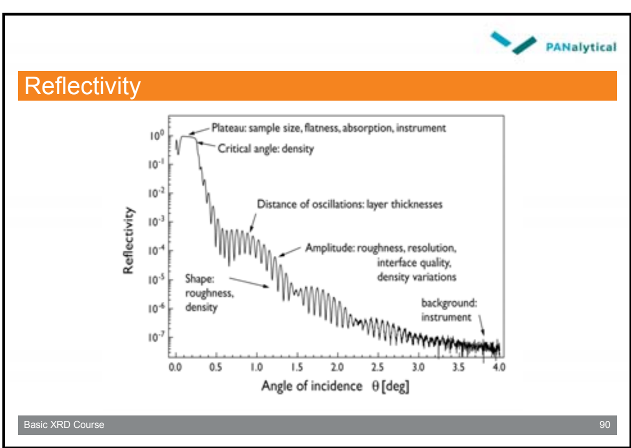
PANalytical
Reflectivity
Plateau: sample size, flatness, absorption, instrument
Critical angle: density
Distance of oscillations: layer thicknesses
Amplitude: roughness, resolution, interface quality, density variations
Shape: roughness, density
background: instrument
Reflectivity
Angle of incidence θ [deg]
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